

Task 2

Drainage Water Treatment

Final Report

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Drainage Water Treatment Technical Committee

The San Joaquin Valley Drainage Implementation Program

and

The University of California Salinity/Drainage Program

Please note that this technical report
is being considered by a publishing company
for possible publication in a book in the near future.

DISCLAIMER

This report presents the results of a study conducted by an independent Technical Committee for the Federal-State Interagency San Joaquin Valley Drainage Implementation Program. The Technical Committee was formed by the University of California Salinity/Drainage Program. The purpose of the report is to provide the Drainage Program agencies with information for consideration in updating alternatives for agricultural drainage water management. Publication of any findings or recommendations in this report should not be construed as representing the concurrence of the Program agencies. Also, mention of trade names or commercial products does not constitute agency endorsement or recommendation.

The San Joaquin Valley Drainage Implementation Program was established in 1991 as a cooperative effort of the United States Bureau of Reclamation, United States Fish and Wildlife Service, United States Geological Survey, United States Department of Agriculture-Natural Resources Conservation Service, California Water Resources Control Board, California Department of Fish and Game, California Department of Food and Agriculture, and the California Department of Water Resources.

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Drainage Treatment Technical Committee Report

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San Joaquin Valley Drainage Implementation Program

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Advanced Treatment Technologies in the Remediation of Seleniferous Drainage Waters and Sediments

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This review identifies and evaluates research findings on various treatment options for selenium removal and disposal of salts in the San Joaquin Valley, California. Selenium from agricultural drainage water has the potential to bioaccumulate at high enough levels in plants and animals so as to cause mortality and to impair reproduction of fish and aquatic birds. The selenium link between agricultural drainage and impacts on birds was first documented in 1983 by U.S. Fish and Wildlife Service studies at Kesterson Reservoir in the SJV. Aquatic plants, invertebrates, fish, frogs, snakes, birds and mammals at Kesterson Reservoir contained elevated selenium levels, often averaging a 100-fold increase over samples collected for similar species at reference sites (Ohlendorf, 1989; Ohlendorf and Santolo, 1994).

I. REGULATORY PERSPECTIVE OF TREATMENT TECHNOLOGIES FOR SUBSURFACE AGRICULTURAL DRAINAGE WATER

The treatment of subsurface agricultural drainage water has several regulatory considerations. The goals or objectives of treatment technologies can be categorized as: (i) reduce constituents below hazardous levels, (ii) meet agricultural water quality goals, (iii) meet water quality objectives in surface waters, and (iv) reduce constituents below risk levels for wildlife.

The first goal of drainage water treatment is to reduce constituents below hazardous levels. The two most common elements in drainage water that approach hazardous levels are selenium and arsenic. In some subareas (e.g., Westlands), drainage water contains levels of selenium that approach the numeric criterion defining hazardous waste. This level is defined in Title 22, California Code of Regulations. Selenium levels above 1,000 $\mu\text{g/L}$ and arsenic levels above 5,000 $\mu\text{g/L}$ are considered hazardous. The use of treatment technologies to reduce constituent levels below hazardous criteria would be appropriate in: (i) areas with high selenium levels; (ii) areas with high arsenic levels; (iii) areas where reuse of drainage water (e.g., agroforestry) concentrates trace elements above numeric criteria defining hazardous waste; and (iv) where required to allow disposal of the water to a river or stream.

The second goal for meeting agricultural water quality standards is applicable to all subareas. Treatment of drainage water to be reused for agricultural supply would require reducing boron (700 $\mu\text{g/L}$) and salt (TDS = 450 mg/L and EC = 700 $\mu\text{S/m}$) levels to meet agricultural water quality goals (Ayers and Westcot, 1985) or reduce the boron and salt levels sufficiently to allow blending with a better quality water supply. These agricultural water quality goals would not be applicable as a regulatory number to manage drainage at the farm level.

The third goal of meeting water quality objectives is applicable to surface water discharges. The primary discharge of drainage water is to the San Joaquin River, California, although some drainage water is discharged to the Kings River and other surface waters. Water quality objectives for selenium and salts are established for the San Joaquin River and listed in The Water Quality Control Plan for the Sacramento River Basin and the San Joaquin River Basin, Third Edition and Amendments (RWQCB, 1994). In the year 2010, the water quality objective in the San Joaquin River for selenium concentration will be 5 µg/L (based on 4-day average). The objective for salinity in the San Joaquin River at Vernalis is an electrical conductance (based upon a 30-day running average) of 700 µS/m from April to August and 1,000 µS/m September to March. Also, drainage discharge to the Kings River in the Tulare Lake Basin may occur provided water quality objectives are met and beneficial uses are not impaired (The Water Quality Control Plan for the Tulare Lake Basin, 1995). Discharge to the Kings River must have an electrical conductance below 1,000 µS/m, boron level below 1 mg/L, and chloride level below 175 mg/L.

The fourth goal, reducing constituents below risk levels for wildlife, would apply to primarily any open body of water containing elevated levels of selenium (≥ 2 µg/L). This standard would include not only evaporation basins but also drainage water storage basins. The subareas would include: (i) the Tulare and Kern subareas for evaporation basins and (ii) the Grasslands subarea for drainage water storage basins. Treatment technologies would need to reduce the selenium levels to about 2 µg/L or isolate the mechanism for bioaccumulation to eliminate risk to wildlife associated with selenium. Currently, operators of evaporation basins with a geometric mean selenium concentration greater than 2 µg/L are required to analyze egg selenium levels (egg selenium is a better indicator of wildlife impact than water selenium). If egg selenium levels are elevated then mitigation habitat must be provided. Selenium treatment technologies must consider the potential of mitigation habitat when selenium levels exceed 2 µg/L.

Treatment technologies currently being evaluated to reduce the selenium load in drainage water include physical, chemical and biological methods. There are three recent books that provide worldwide compilation of scientific studies related to the treatment technologies of selenium, edited by Jacobs et al. (1989), Frankenberger and Bensen (1994), and Frankenberger and Engberg (1998). A detailed discussion of drainwater treatment methods, field trials and relative costs was the focus of a report by Hanna et al. (1990), submitted to the San Joaquin Valley Drainage Program, Sacramento, California. This report will focus on ion exchange, reverse osmosis, solar ponds, chemical reduction with iron, microalgal-bacterial treatment, volatilization, biological precipitation, and flow-through wetlands as viable technologies.

II. TREATMENT TECHNOLOGIES

A. Ion Exchange

Ion exchange involves the exchange of an undesirable dissolved constituent for a more desirable solute electrostatically attached to an ion exchange material. This material is often a synthetic resin, but for the purposes of this discussion may also include a naturally occurring zeolite or activated alumina. While ion exchange is used for desalting water (deionized water is commonly used in industry), it is generally uneconomic for treatment of agricultural drainage when compared with reverse osmosis. In fact, most industries have upgraded their deionized water facilities by providing reverse osmosis as a pretreatment, followed by an ion exchange system to polish the water to extremely low TDS levels. However, ion exchange is often used for specific ion removal rather than overall salinity reduction. Examples include the nitrate removal facilities found at McFarland and other California cities. Ion exchange systems find widespread use for water softening in the removal of calcium and magnesium (hardness reduction).

Ion exchange resins can selectively remove a specific ion in preference to others. Recent research has shown that resins are suitable for targeting arsenic, selenium and other ionic constituents. However, since selenate (the common form of selenium in drainage water) and sulfate have very similar chemical properties, it is difficult to separate selenate (at the parts per billion concentration) from sulfate (at the parts per million concentration) since a resin would quickly become saturated with sulfate ions and stop removing selenate. Research performed at the Panoche Water District has demonstrated that at least one commercially available resin is capable of removing selenate ion even when saturated with sulfate. The selenate ion was primarily removed at low concentrations.

Sometimes, selective ion removal can be accomplished by properly pretreating the drainwater. For example, arsenic can be present in several ionic forms, depending upon the pH and oxidation state (pE) of the water. At certain pH and pE ranges, arsenic is in the arsenious acid form, and will not be removed by ion exchange. When the water is oxidized (e.g. by addition of chlorine) and the pH properly adjusted, arsenic is converted to arsenate ion, which is readily removed by ion exchange in preference to many other common ions. Thus, appropriate pretreatment may be the key to economical application of using ion exchange for selective removal of a specific contaminant.

Ion exchange is a very simple process to operate and is suitable for intermittent flow. Labor requirements are low, typically requiring an hour a day to monitor the condition of the equipment. Ion exchange produces a salty waste stream, typically to 1 to 5 percent of the product water. This waste contains material removed from the treated water, as well as unused salt from the regeneration process. Disposal often requires evaporation and landfilling of the precipitated salts, although it is possible that in certain cases the waste may be useable for some beneficial purpose. When used for specific ion removal, ion exchange is relatively inexpensive on both a capital and operating cost basis when compared with other processes. The regenerable nature of the treatment medium helps to distribute the purchase cost over the long term. An ion

exchange treatment system can be expected to have a capital cost in the range of \$0.30 to \$0.50 per gallon per day capacity, depending upon the need for specialized pretreatment. Operating and maintenance costs can be expected to range from \$30 to \$100 per acre foot of water.

The capital cost of ion exchange equipment is less than for reverse osmosis or distillation equipment. However, the cost of regenerating chemicals for waters with a TDS over a few hundred mg/L generally make ion exchange economically unattractive for demineralizing water when the “total water cost” (capital and operation and maintenance costs) are considered. But, the use of ion exchange for specific ion removal, such as selenium, holds promise and should be considered.

B. Distillation Processes

Distillation processes, as the name implies, rely on evaporation and condensation to demineralize water. While distillation processes are used to desalt sea water, energy consumption is substantially more, for example, than sea water desalting using reverse osmosis. In addition, the capital cost of distillation plants is usually more than for reverse osmosis. The cost of distillation would be prohibitive when applied to brackish irrigation drainage waters since energy consumption is not related to salinity. For example, distillation of seawater at 35,000 mg/L would cost essentially the same as application of this treatment to drainage water at less than 10,000 mg/L.

Distillation processes are mentioned here because they could be used to demineralize irrigation drainage water. However, as noted above, they are almost without exception more expensive than reverse osmosis except for locations where energy is inexpensive, such as in Saudia Arabia, where large supplies of natural gas are available and where sea water desalting plants have been built as part of a “dual purpose” facility; i.e., power generation and water production.

C. Membrane Processes

There are several membrane water treatment processes:

- Microfiltration—a solids (particulate) removal filtration process with membrane pore sizes of about 0.2 μm . Microfiltration does not remove dissolved substances from water but can be used to pretreat (remove solids) from water for further treatment by a desalting process.
- Ultrafiltration—a solids removal filtration process similar to microfiltration except the membrane pore size is about 0.02 μm .
- Nanofiltration—a reverse osmosis process sometimes called “membrane softening.” Nanofiltration will remove dissolved substances from water and is especially effective for removing divalent ions such as calcium, magnesium and sulfate hence the name “membrane softening”.

- Reverse osmosis (hyperfiltration)—a dissolved substances removal process that is also very effective at removing monovalent ions, such as sodium, chloride, etc., as well as divalent ions from water.
- Electrodialysis—a membrane process that is used to remove electrically charged dissolved substances from water.

Micro- and ultrafiltration are solids removal membrane processes and this discussion concerns removal of dissolved substances from water. They are mentioned here only because they might find application in pretreating irrigation water by a dissolved solids removal process (reverse osmosis, ion exchange, or nanofiltration).

There are two primary differences between the reverse osmosis processes (nanofiltration and hyperfiltration) and electrodialysis; what passes through the membranes and the driving force. In reverse osmosis the water passes through the membranes. The “rejected” salts (salts and other dissolved substances) remain on the feed water side of the membrane (the “concentrate side”). The water passes through the membrane to the “permeate side” The driving force is pressure.

In electrodialysis, the electrically charged ions pass through the membranes, not the water as in reverse osmosis. The driving force in this case is electric potential (voltage).

While both reverse osmosis and electrodialysis can be used to demineralize irrigation drainage water, electrodialysis is usually somewhat more expensive than reverse osmosis, especially when the TDS exceeds about two or three thousand mg/L. Energy consumption of both processes is directly related to the feed water salt content. Studies have shown, given environmental constraints and the current level of technology, that reverse osmosis usually provides lower costs for desalting brackish water. In previous demonstrations with agricultural drainage, reverse osmosis has been favored over electrodialysis.

Reverse osmosis is applicable to natural waters over a wide salinity range whereas electrodialysis is generally restricted to salinity levels of 15,000 mg/L or less. Energy consumption of both processes is directly related to the feed water salt content. Studies have shown, given environmental constraints and the current level of technology, that reverse osmosis provides substantially lower costs for desalting even seawater. For brackish water, this process is especially attractive. In previous demonstrations with agricultural drainage, reverse osmosis has been favored over electrodialysis.

Reverse osmosis is a “broad spectrum” treatment process capable of removing numerous contaminants. In this technology a semipermeable membrane selectively allows the passage of solvent (water) while rejecting the solute (dissolved salts and organics). Osmosis is a term describing the natural tendency of a system to equalize solute concentration on both sides of a semipermeable membrane as solvent migrates through this barrier from low to higher solute concentration. Reverse osmosis, then, reverses the natural osmotic process by applying pressure to the solution with higher solute concentration. In this manner, pure solvent is forced through the membrane.

Pressures required to drive this process must exceed the osmotic pressure of the saline water being treated.

Early reverse osmosis membranes were developed from asymmetric cellulose acetate films (Loeb and Sourirajan, 1960). This material is still in use, however, performance is limited and cellulosic derivatives are easily fouled by bacterial growth on the membrane surface. Other polymeric materials and fabrication techniques rapidly followed the “first” reverse osmosis membrane (Petersen, 1993). These “new generation” membranes show dramatically higher levels of salt rejection and product water recovery at a given driving pressure. A widely used class of high performance membranes are generally referred to as thin film composite (TFC). They are formed by casting a thin polymeric film onto a porous substrate composed of several layers of various materials. Many different types of TFC membranes are available and are rated according to their pressure requirements, flux characteristics and capability of salt rejection (typically 95 to 99.7 percent).

Higher rejection membranes generally require higher pressures to provide a given product water flux. However, great strides have been made during the past few years in improving the pressure-flux characteristics of membranes while maintaining excellent salt rejection. A recently developed high performance TFC type of membrane known as nanofiltration (NF) has shown some interesting performance characteristics. These films, also known as softening membranes, operate at remarkably low pressures, providing reasonable overall salt rejection but have been designed to selectively reject divalent ions.

While there are differences in rejection of various ions, they are relatively minor. For example, a given membrane may show a rejection of 99 percent for nitrate but only 96 percent for chloride. Membranes generally reject multivalent ions better than univalent and any charged particle better than an uncharged species. Rejection of dissolved organic compounds can vary widely and depends on the size and structure of the organic molecule.

If the dissolved ions in the water are primarily divalent ions (calcium, magnesium, and sulfate) nanofiltration membranes may be better suited for desalination of agricultural drainage waters than reverse osmosis membranes. If, however, there is a large percentage of monovalent ions in the water (sodium and chloride, for example) then reverse osmosis membranes may be more suitable. While nanofiltration membranes used to have a substantial advantage over reverse osmosis membranes with respect to operating pressure (energy consumption), the development of “ultra low pressure” reverse membranes in the last few years has largely narrowed the former energy consumption advantage of nanofiltration membranes.

Depending on the membrane type, salt rejections up to 99 percent are routinely observed with reverse osmosis. If the TDS of the irrigation water is, for example, 10,000 mg/L, the permeate may have a TDS of only about 100 mg/L. Membranes generally reject multivalent ions better than univalent and any charged particle better than an uncharged species. Rejection of dissolved organic compounds can vary widely and depends on the size and structure of the organic molecule.

The impact of membrane fouling must also be carefully considered in the design of any membrane desalination plant. Fouling may result from feed waters containing particulate matter, potential scale forming ions, dissolved organics or micro-organisms. Depending on the source water quality, design of pretreatment systems is of crucial importance.

The recovery (percent of feed water “recovered” as permeate) from a membrane plant depends on several factors including water chemistry, membrane configuration, and design of pretreatment systems. The latter factor is of crucial importance since most agricultural drainage waters contain very high levels of calcium and sulfate ions which can readily precipitate gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) on membrane surfaces as product water recovery increases. Addition of scale inhibiting chemicals to feed water provides for operation at higher rates of recovery.

A reverse osmosis plant treating drainage water with TDS levels below about 10,000 mg/L can be expected to have a capital cost of about \$2.00 per gallon per day of capacity. If extensive pretreatment (to remove solids from the reverse osmotic feed water) is required, the cost may rise an additional \$1.00 per gallon per day of capacity. Operating costs can be expected to range between \$150 and \$300 per acre foot depending on feed water quality. A recent study on drainage water desalting costs completed for the Buena Vista Water Storage District developed a water cost of about \$300 per acre foot, including capital repayment (20 years at 7 percent) and O&M cost. This figure did not include the cost of facilities to gather the drainage water, dispose of the waste, or deliver the treated water. In another study on softening of well water in Florida (Bergman, 1996), costs of nanofiltration membrane treatment ranged between \$2.05 and \$3.05 per 1,000 gallons. This overall cost included amortized construction and O&M.

The first attempt at drainage water reclamation began in 1971 at Firebaugh, California (McCutchan et al., 1976). A small membrane pilot plant utilizing hand-cast cellulose acetate tubular membranes was designed and built at the UCLA School of Engineering and Applied Science. The plant remained on-line for approximately three years and was operated jointly by UCLA and the California Department of Water Resources. Water quality at this site varied in TDS levels between 2,000 and 7,000 mg/L and calcium and sulfate ion concentrations near saturation with respect to gypsum. A limiting issue in processing this water was the potential deposition of scale on membrane surfaces. Scale control was effected first by treatment with sodium hexametaphosphate followed by installation of a cation exchange system for calcium removal. Product water recovery based on chemical and ion exchange treatment, were reported at 60 percent and 90 percent respectively. Adequate levels of product water flux and overall salt rejection were also reported but usual operating pressures ranged between 600 and 900 psi.

Feasibility of this technology in drainage water reclamation was clearly demonstrated at Firebaugh but cost effectiveness was limited by the very high pressure requirements of the cellulose acetate membranes available at that time. It should be noted that the advancement in reverse osmosis membrane technology in the last few years has resulted in membranes that operate at pressures of about 1/3 of those experienced at Firebaugh. It should also be noted that construction and operation of ion

exchange systems would place another large economic constraint on membrane desalination of SJV drainage water.

The next phase in membrane applications took place at Los Banos between 1983 and 1987 (Smith, 1992). This sophisticated installation incorporated a number of novel pretreatment strategies and was tied in with solar pond development which provided a “sink” for brine disposal and utilization of solar energy. Membranes installed at this facility were provided by three leading manufacturers and represented typical reverse osmosis (RO) technology available at that time. Regretfully this site was shut down in 1986 following the discovery of environmentally hazardous levels of selenium at the Kesterson Reservoir. Although the reverse osmosis units operated for relatively short periods, overall performance, once again, demonstrated the potential feasibility of membrane desalination for agricultural drainage water treatment.

Further studies on membrane desalination with “new generation” nanofiltration (NF) membranes show high levels of salt rejection while operating at remarkably low pressures. Performance parameters of these membranes have been evaluated with “model solutions” simulating the composition of drainage water at the Adams Avenue Agricultural Drainage Water Research Center. At applied pressures less than 200 psi, product water flux (gallons per day per square foot of membrane area – GFD) and salt rejection were measured at levels up to approximately 18 GFD and 90 percent respectively. Such data tend to forecast much lower product water costs compared with technology available in the early 1980's.

Currently, research efforts are focused on potential gypsum scaling which is a critical issue in the design of pretreatment for a membrane desalination facility (LeGouellec et al., 1997). Work to date shows encouraging results with some of the leading commercial antiscalants. Goals are directed toward development of a pilot plant with performance levels equal to or exceeding those measured in the laboratory and capable of product water recovery at approximately 70 percent.

At this time hard data is not available to adequately provide for an economic assessment of agricultural drainage water desalination by membrane processes but following is a list of factors both positive and negative which would influence the planning of membrane treatment facilities.

POSITIVE

1. NF membranes demonstrate remarkable efficiency for potential drainage water treatment in comparison with the best membranes available in the early 1980's when design specifications for the Los Banos facility were under development.
2. Brine generated from membrane treatment will have an overall ionic concentration approximately three times ambient drainage water. The enhanced selenate levels should facilitate the efficiency of proposed bioremediation and phytoremediation schemes. However, the impact of increased salinity on biological processes is presently unknown.

3. Reduced brine volumes will simplify the design of evaporating ponds and/or provide concentrated solutions for solar ponds if this technology is re-considered.
4. Product water reclamation as an augment to imported irrigation water should be factored in to an economic assessment of membrane technology.

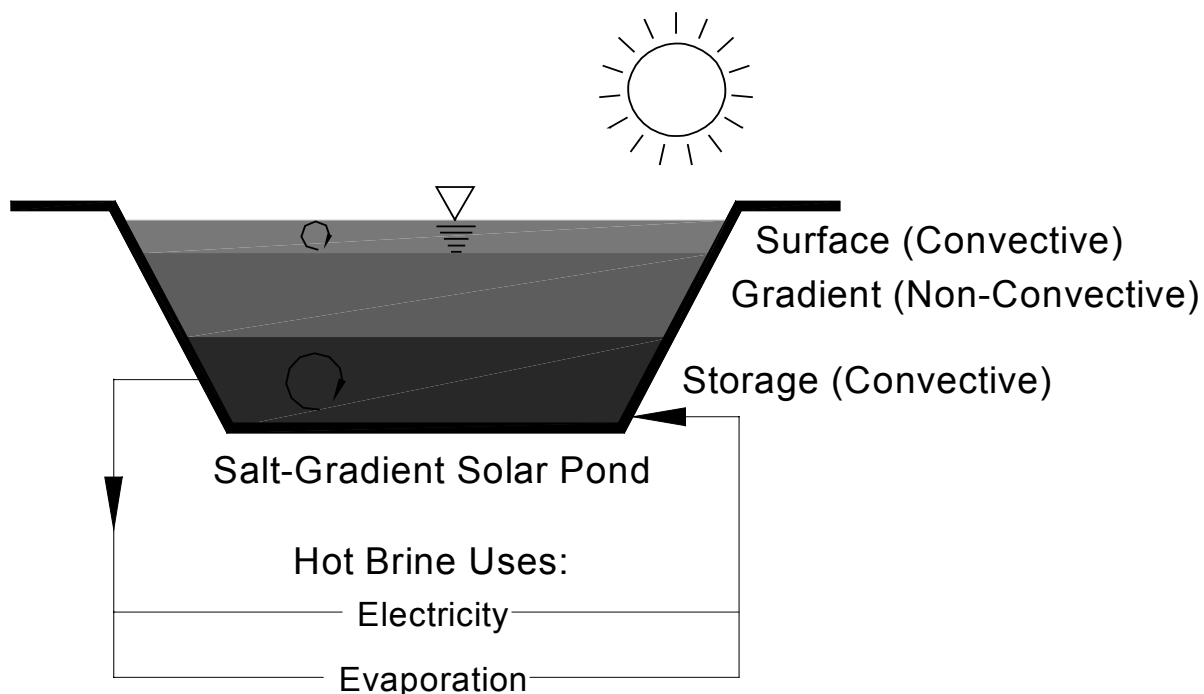
NEGATIVE

1. Little information is available at this time to assess the durability and life expectancy of NF membranes.
2. In addition, little information is available to assess the sensitivity of NF membranes to disinfectants.
3. Some research has been conducted on trace organics in feed water but not enough to completely assess the impact of measured TOC levels on membrane performance.

D. Solar Ponds

The use of salt-gradient solar ponds may play an important long-term role in drainage treatment for regions of the SJV. Solar ponds provide an environmentally safe method for storage of agricultural drainage water salts and an alternative source of energy. A large quantity of salt is required to construct a solar pond. It takes the amount of salt in 146 acre-ft of 10,000 mg/L TDS drainage water to create one acre of solar pond with gradient and storage layers of 5 feet each. Agricultural drainage water is concentrated 32 times for use in the storage zone of a solar pond.

Salt-gradient solar ponds are bodies of water in which the salinity at the bottom is greater than the salinity at the surface. Depth may range from a fraction of a meter to several meters. Normally, as shown in the figure below, solar ponds consist of three zones: a relatively homogeneous and convective surface layer; a non-conductive gradient zone in which there are gradients in salinity and temperature; and a homogeneous and convective bottom zone. The non-convective gradient zone transfers heat by conduction only, water being opaque to thermal radiation at the temperature of operation. It thus acts as a partially transparent window of low thermal conductivity that allows some solar radiation to penetrate and heat the bottom zone. The gradient remains gravitationally stable and non-convective despite, the heating of the bottom because the salinity gradient is sufficient to maintain a stabilizing density gradient (Dickinson and Cheremisinoff, 1980).



The California Department of Water Resources, at its Demonstration Desalting Facility in Los Banos, California, has investigated the use of a salt-gradient solar pond to treat agricultural drainage water from 1985 through 1989. The half-acre pond generated temperatures in excess of 180°F (82°C) (Engdahl, 1987). This investigation demonstrated the use of the storage zone's heat to generate electricity with a Rankine-cycle engine. The use of the heat directly as the driving force for evaporation in a vertical tube evaporation process was also demonstrated (Kovac, 1990).

The solar pond should be viewed as an integrated system to reclaim or concentrate agricultural drainage, store brine, and separate solid salts. Some processes being developed to treat and concentrate drainage water and separate salts will be employed in this "solar pond" system. Work is needed to develop operating guidelines, provide reliable estimates of potential energy production, and evaluate critical economic factors. Additional work is needed to understand how these systems prevent selenium in the water column from entering the food chain.

E. Chemical Reduction of Selenium with Zero-valent Iron

Iron filings (zero-valent iron) can be used to remove selenium from water. The iron acts as both a catalyst and reductant (electron donor) for the reaction. The selenium is reduced to selenite, Se(0) , and selenide depending upon pH and O_2 of the water. Low pH and low oxygen favors the more reduced forms of selenium. In 1985, Harza Engineering Co. tested a pilot-scale processes using iron filings in flow-through beds. The testing was discontinued because the beds quickly cemented with precipitates. The study did not conclusively identify the oxyhydroxide precipitates but recent work suggests that "green-rust" ($\text{Fe}^{\text{II}}_4\text{Fe}^{\text{III}}_2(\text{OH})_{12}\text{SO}_4 \cdot n\text{H}_2\text{O}$) may be the initial precipitate, which is then oxidized to magnetite (Fe_3O_4) by nitrate and oxygen (Hansen, et al. 1996). Other likely precipitates include siderite (FeCO_3) and ferrihydrite [$\text{Fe}(\text{OH})_3$]. The advantage of zero-valent iron is it can reduce the concentration of Se to very low concentrations and might be useful as a polishing step following microbial

treatments. If the wastewater is anaerobic as a result of the microbial treatment, the formation of secondary precipitates is minimized.

F. Chemical Reduction of Selenium with Ferrous Hydroxides

A chemical reduction process for removal of selenate from subsurface agricultural drainage was developed and studied by the USBR Engineering and Research Center, Denver, Colorado. Chemical reduction occurs between selenate and ferrous hydroxide under alkaline conditions, producing iron oxides and elemental selenium, which are then removed by gravity settling.

USBR conducted bench level and batch reactors at their Denver laboratory and found that selenate enriched synthetic drainage water was reduced to less than 5 µg/L within one minute. These initial studies were followed in the field with a micro-pilot plant at Murietta Farms, Mendota, CA using SJV drainage water. Field studies indicated slower rates of reactions. Although up to 90 percent of selenate was reduced, nearly 6 hours reactor time was needed. It was found that dissolved oxygen, nitrate and bicarbonate interfered with the reduction process. Dissolved oxygen consumed excessive ferrous hydroxide while nitrate and bicarbonate retarded the rate of reaction. Pretreatment of drainage water with sulfur dioxide can reduce dissolved oxygen and bicarbonate interference, but nitrate reduction was costly using chemical or physical methods. Without nitrate interference, drainage treatment by this technology is projected to cost about \$150 per acre-foot.

USBR has completed construction of a continuous flow reactor with pre-treatment devices, followed by ferrous hydroxide reduction. However, nitrate reduction is required for this treatment technology to be an economical process. USBR has investigated innovative nitrate removal processes that are promising, but need further development. At present, USBR budget constraints and priorities have delayed further progress on this technology.

The goal for selenium reduction is to achieve local receiving water standards (5µg/L) and this would require more than 99 percent reduction of the typical drainage water. However, present basin management is directed to selenium load reduction. This shift in basin management approach would provide opportunity for processes that are less costly in achieving load reduction, without meeting the stringent receiving water standards that are based on concentrations. Chemical reduction of selenate with ferrous hydroxide in subsurface drainage can be achieved but will not meet the very low standard levels due to nitrate interference. Further studies are needed to control nitrate interference at a reasonable cost.

G. Algal-Bacterial Selenium Removal Process

W.J. Oswald and his Applied Algae Research Group at the University of California, Berkeley have developed a selenium treatment process consisting of a series of specially-designed ponds. This group operated a 760-gallon per day prototype Algal-Bacterial Selenium Removal (ABSR) system near Mendota from 1986 to 1989. The best reductions in total soluble selenium were from 400 µg/L to less than 10 µg/L. Preliminary economic analyses conducted in 1988 indicated that ABSR facilities with

capacities of 3, 30, and 300 acre-feet per day would have a total costs of \$272, \$103, and \$68 per acre-foot, respectively. The Mendota studies elucidated several key microbiological and physico-chemical mechanisms for selenium and nitrate removal and laid the foundation for a current 10,000 to 20,000 gallon per day demonstration project (Lundquist *et al.*, 1994).

ABSR Basics. The concept of the ABSR Process is to grow microalgae in drainage water at the expense of nitrate and then to utilize the naturally-settled algal biomass as a carbon source for native bacteria which, in the absence of oxygen, reduce the remaining nitrate to nitrogen gas and reduce selenate to insoluble selenium. The insoluble selenium is then removed from the water by sedimentation in deep ponds and, as needed, by dissolved air flotation and sand filtration. Supplemental carbon sources such as molasses can be employed as reductant in addition to algal biomass.

Past and current studies show a clear need to reduce dissolved oxygen and nitrate to low levels before selenate can be reduced. In the ABSR Process this reduction is carried out by bacteria in Reduction Ponds (RPs) that are sufficiently deep and/or covered to exclude oxygen. Nitrate is also removed by assimilation into algal biomass in High Rate Ponds (HRPs). Since nitrate concentrations in drainage water are often as high as 90 mg/L as N compared to <0.5 mg/L for selenium, the carbon requirement for nitrate reduction far exceeds that for selenium reduction. According to the experience of Oswald's group, the high sulfate concentration (2,000 to 4,000 mg/L as SO_4^{2-}) in drainage water does not appear to significantly interfere with nitrate or selenium reduction.

Selenium removed from the water column accumulates in settled algal-bacterial biomass and inert materials in the bottom of the RPs. Because the biomass is continuously undergoing anaerobic decomposition, the volume of solid residues increases slowly. Removal and disposal of the solids in a landfill should not be required until after many years of accumulation. Alternatively, the dried inert solids which contain nitrogen, phosphorus, and selenium could be useful as a soil amendment and fertilizer in the eastern Central Valley where the soils are selenium deficient.

Large-scale ABSR Facilities are expected to pose much less hazard to wildlife than the surrounding drainage channels or evaporation ponds. The concentration of selenium in the shallow HRPs will be similar to or less than that of the drainage channels themselves, and HRPs are continuously mixed by paddle wheels to prevent sedimentation of particulates. Concentrated selenium will be sequestered in the anaerobic depths of the RPs. At 16- to 20-foot depth, the anaerobic RP floor cannot support invertebrate life and will not attract waterfowl.

Panoche Facility. The objective of the project hosted by the Panoche Drainage District is to demonstrate the technical and economic feasibility of the ABSR Process for reduction of selenium loads from a portion of the combined drainage flows of several districts or from selected drainage sumps within a single district.

The ABSR Facility consists of two identical ABSR systems treating a total of 10,000 gallons per day as of October 1998. Different sequences of nitrate removal are being evaluated in each system. The Mode 1 system assimilates part of the nitrate in

HRP algae and denitrifies the rest using algae as the bacterial substrate, while the Mode 2 system depends entirely on denitrification fueled by molasses and algal substrates.

Under Mode 1, the HRP has removed an averaged 50 mg/L $\text{NO}_3\text{-N}$ during March to October 1998. Denitrification of the residual nitrate has been complete from August to October 1998. Denitrification in the Mode 2 system has consistently reduced nitrate-N from over 70 mg/L to less than 10 mg/L as N during April 1997 to October 1998 except for February and March 1998 when impassable roads prevented RP substrate feeding.

Over 99 percent of the selenium in the drainage water influent is in the selenate form (SeO_4^{2-}), but the raw pond effluents are a mixture of selenate, selenite (SeO_3^{2-}), and particulate selenium. As needed, particulate- and selenite-selenium can be removed from the pond effluents with iron salt coagulation followed by clarification and filtration. Selenate concentrations in the influent and effluents of the pond systems are currently used to determine selenium removal efficiencies.

The Mode 1 system reduced selenate concentration by 49 percent from March 1998 through August 1998. The lowest concentrations were 39 $\mu\text{g/L}$ selenate-Se and 93 $\mu\text{g/L}$ total soluble selenium. Since January 1997, the Mode 1 system removed 37 percent of its cumulative selenate-Se mass load.

Selenate concentration dropped across the Mode 2 system by an average of 83 percent from July 1997 through January 1998 and, after molasses feeding recommenced, by 94 percent from April through August 1998. During the last period effluent selenate averaged 29 $\mu\text{g/L-Se}$ with a low of 15 $\mu\text{g/L-Se}$. Total soluble selenium averaged 41 $\mu\text{g/L}$. Cumulative selenate-Se mass removal has been 86 percent since January 1997.

The Mode 2 system has given predictable removals for over a year and will now be stress-tested by increased flow during the cooler winter months. During 1998, selenium and nitrate removal in the Mode 1 system has greatly improved, indicating that the cultures of algae and bacteria have matured. This system will continued to be monitored under steady flow until removal rates stabilize.

Once stabilized, operating parameters such as flow rate, pond depth, and nutrient feed rates will be systematically adjusted to determine the conditions that minimize the cost per mass of selenium removed. The main cost components to be reduced are supplemental carbon feed (molasses) and pond volume. Preliminary results indicate that full-scale ABSR facilities will require 4 to 6 acres per acre-ft/day treated. The planned research efforts will provide better information on the costs of selenium load reduction using full-scale ABSR facilities.

H. In Situ Treatment Utilizing Aquatic Algal Productivity

The term "in situ" refers to any open (instead of enclosed) on-site setup while "aquatic algal productivity" refers to any fully aquatic, light-driven biological process, where direct light input is required for part of the process. Thus, "algal" in this section is not restricted to photosynthetic organism or to single-species processes. This broad definition was adopted in order to cover the widest range of current and past technologies and research efforts in this area. In the SJV evaporation ponds, the principal purpose of remediation has been - and still is - alleviating the foodchain ecotoxic effects of selenium in the ponds. Waterborne and sediment Se bioaccumulates readily into the aquatic biota (from primary producers to aquatic birds and top predators) with concentration factors of 1,000 or higher (Ohlendorf, 1997; Maier and Knight, 1994). The extent of bioaccumulation depends on the route of exposure (e.g. diet, water, or sediment) and chemical form of Se (Besser et al., 1993; Maier and Knight, 1994). In Se-laden aquatic environments, chronic toxicity resulting from dietary Se uptake through the foodchain represents a far greater problem than acute toxicity associated with direct water exposure (Maier and Knight, 1994). This chronic Se toxicity is, to an extent, related to the combination of waterborne Se concentration and Se bioaccumulation, as revealed at Kesterson Reservoir and other evaporation basins of the San Joaquin Valley (Skorupa and Ohlendorf, 1991).

However, this relationship is not applicable to all aquatic environments and many cases have been reported where waterborne Se concentrations, Se bioaccumulation, and biological impacts did not correlate (e.g., Hamilton, 1997; Hamilton et al., 1997; Canton and Van Derveer, 1997; Lemly, 1993; Adams et al., 1997). Possibly along similar lines in the SJV, a large decrease in Se content in avian eggs was recently observed at the Rainbow Ranch evaporation pond (Kern County, CA) after a moderate dilution of waterborne Se concentration with agricultural tail water (Anthony Toto, CVRWQCB, Des Hayes, CDWR, and Joe Skorupa, USFWS, personal communication).

Consequently, there is a general consensus (Adams et al., 1997) that the complex Se biogeochemistry, particularly biotransformed Se forms in food organisms, may be the key to chronic Se effects expressed in species such as fish and birds. Since Se biogeochemistry varies with site conditions (e.g. fast-flowing river versus slow-flowing wetlands), Adams et al. (1997) expressed the need for site-specific water quality criteria. Moreover, a departure from using waterborne concentrations (that is, using sediment-based water quality criteria) has also been proposed by Canton and Van Derveer (1997). Cautions regarding the indirect connection of waterborne Se to ecotoxic effects were summarized specifically for Central Valley evaporation ponds by Maier and Knight (1992).

I. Algal Bioremediation Studies

In light of the emerging view that remediation involves complex, site-specific Se biogeochemistry, algal bioremediation efforts in the SJV evaporation ponds appear to be in their infancy. Although there are several algal studies with the stated goal of selenium removal from water, it is clear from the preceding discussion that remediation involves far more than removal; the very definition of "remediation" requires that a process must reduce the factor(s) controlling the ecotoxic effects of selenium.

Recent algal studies at U.C. Davis, which have the long-term goal of alleviating ecotoxic effects, have begun to survey the selenium biogeochemistry of naturally-occurring algae in SJV evaporation ponds (Fan et al., 1997). Their goal is to understand the pathways and control points of ecotoxic effects in order to promote or reduce specific algal processes, as appropriate to foodchain accumulation of selenium. An additional advantage of keying on the naturally-occurring algae is that they are already adapted to the physical-chemical conditions and variations of the SJV evaporation ponds.

Several species of microalgae isolated from SJV evaporation ponds transform selenium oxyanions into volatile alkylselenides, selenonium ions, and proteinaceous selenomethionine (Fan et al., 1997; Fan et al., in press). In particular, two cyanophyte strains isolated from the evaporation basins of the Tulare Lake Drainage District (TLDD) were very active in selenium volatilization. Up to 70 percent of the selenium was depleted from the medium containing 20-1,000 µg/L selenium by the algal activity and a major fraction of the selenium loss was accounted for via the volatilization route. It is possible that the algal selenium volatilization activity may be related to the recent observation that waterborne selenium concentrations at one of the TLDD basins were not increasing with rising salinity and that this trend was consistent year-around (Doug Davis, personal communication). The same observation was noted at Kesterson Reservoir by Saiki and Lowe (1987) and Schuler (1987). Selenium concentrations generally were reduced from the San Luis Drain through a series of ponds, whereas TDS and boron increased through evapo-concentration. Additional research is needed to determine this relationship. Moreover, selenium volatilization and depletion from water were significantly enhanced by a sudden drop of the medium salinity. How this salinity-induced change in selenium fate is related to the substantial drop in selenium concentration in avian eggs collected from the Rainbow Ranch evaporation pond is unclear. One possibility is that the enhancement of selenium volatilization induced by decreased salinity may divert selenium away from bioaccumulation in aquatic birds observed at Rainbow Ranch. Further research will need to be conducted to unravel this potentially important phenomenon.

Thus, it may be possible to further enhance this reduction of selenium accumulation into aquatic birds, if the mechanism(s) underlying the phenomenon is understood. If successful, such a "natural bioremediation" approach should represent a readily implementable and economical means for alleviating selenium contamination problems, not only in agricultural evaporation basins but also in other lentic systems (e.g. reservoirs and lakes) that receive Se-laden industrial waters.

Although selenium volatilization accounted for a major loss of total selenium from water in laboratory studies, a significant amount of selenium was also accumulated in the algae, particularly in proteins where selenomethionine was the dominant form. Moreover, there was a major difference in selenium allocation into proteins among different algal species (Fan et al., in press); the significance of this finding is that the different protein-bound selenium content may represent very different foodchain transfer and ecotoxic potential among algae. This notion is supported by other studies, e.g., where diet with a higher level of protein led to a higher selenium content in fish tissues (Reidel et al., 1997). On the other hand, a higher protein content in water (e.g. from decaying algae) led to dramatically increased selenium volatilization in evaporation pond water by bacteria (Frankenberger and Thompson-Eagle, 1989), but the ecotoxic consequences were not addressed in that study.

At this time, there appear to be no other algal studies that address bioremediation per se in evaporation ponds. The above studies by Fan et al. still have considerable work to be done because the factor(s) that control the ecotoxic foodchain effects of selenium are not sufficiently understood. Consequently, it is not known what practical measurements must be made in order to assess the effectiveness of a process for remediation purposes.

J. Selenium Removal from Water by Algal Processes

Studies of selenium removal from water - without addressing ecotoxic remediation - have shown interesting results. These are treated briefly here.

In 1986, Packer and Knight reported that the cyanobacteria ("blue-green algae") *Synechococcus* 6311 could be used to remove selenium from waters (Packer and Knight, 1986). The mechanism of selenium uptake was proposed to be analogous to that of S uptake, and the selenium was preferentially taken up over S at low sulfate levels, while the opposite was true at high sulfate levels. The remediation potential of the approach was not discussed. This approach was apparently not pursued, possibly due to the high sulfate salinity of evaporation ponds.

Over the last decade, a group based at UC-Berkeley have worked on an algal-bacteria system for selenium removal from water (Lundquist et al., 1994). Very briefly stated, the system uses algae primarily as an organic carbon source for bacteria (*Acinetobacter* sp. and *Pseudomonas* sp.) to reduce the selenium oxyanions to insoluble forms (e.g. colloidal Se^0) that can be removed from water. In its present form (Benson et al., 1997), the focus of the system is on reducing waterborne selenium to meet the discharge requirements into rivers, and does not appear to involve evaporation ponds per se. The algal biotransformation activity was not reported and the remediation potential for ecotoxic risk is unclear.

Nelson et al. (1997) at UC-Davis have developed a laboratory bacterial culture of *Chromatium vinosum* or *Chlorobium limicola* plus *Desulfovibrio desulfuricans* to reduce selenate to selenium-rich intracellular colloids probably containing Se^0 . The process is "algal" under our definition because the first two organisms are grown phototrophically under anaerobic conditions, essential for control of the selenium chemistry. The

authors envision the process as useful in a bioreactor situation to remove selenium oxyanions from the water. The remediation potential of the approach was not discussed.

K. Other Current Work that Includes Algal Processes

In addition to the efforts at algal selenium removal, there are other investigations currently underway that deliberately or incidentally involve algal processes. These are described very briefly here.

Terry (1997) and Tanji (1997) describe a study using outdoor flow-through wetlands for the removal of selenium from water. Because of the open design, including cells which have no vascular plants, the system is intentionally designed to include the effects of algae. As this system has only recently stabilized, there are no clear conclusions that can be drawn at this time.

Parker et al. (1997) are using evaporation pond/wetland mesocosms to track the fate and partitioning of selenium. This is intended to be a more defined study of one described by Terry (1997). Since this is a biogeochemical system, it will involve the action of algae, although there is no intentional inoculation of any species.

L. Criteria for Success of In Situ Biologically Based Selenium Treatment Technology

Simple parameters such as waterborne selenium concentration are not likely to be reliable indicators for success of in situ selenium bioremediation technologies. The main reasons for this are reiterated here: 1) The goal of selenium remediation is to minimize ecotoxic risk, not just removing selenium from waters; 2) selenium exposure and toxicity in birds and fish primarily result from selenium biotransformations and transfer pathways through the foodweb, which are not simple functions of waterborne selenium concentration. Waterborne selenium concentrations much below 5 µg/L (the current EPA selenium freshwater quality criterion) have been shown to have adverse effects on fish (e.g. Lemly, 1993). Conversely, there have been cases where no apparent selenium toxicity was observed with waterborne selenium concentrations much higher than 5 µg/L (e.g. Canton and Van Derveer, 1997; Hamilton et al., 1997).

The consensus conclusion, based on such results, was that waterborne selenium concentrations alone would be inadequate in assessing the selenium impact on the aquatic community (from a 9-member expert panel in a recent "Peer Consultation Workshop on Selenium Aquatic Toxicity and Bioaccumulation" held by the US Environmental Protection Agency, May, 1998). It was clear from the panel discussion that more reliable parameters such as selenium burden in representative tissues and tissue compartments (e.g. proteins) will be needed for selenium impact assessment. In light of these new findings in the last decade, EPA is initiating the process of re-evaluating the current chronic water quality criterion for selenium. More reliable parameters will lead to better regulatory criteria for protecting the aquatic community, and will be equally important for assessing the efficacy of any mitigation measure.

M. Volatilization

Volatilization of selenium, a naturally occurring component of selenium cycling in the biosphere, is a primary mechanism of dissipating various selenium ions out of water and sediments. Comprehensive reviews have been published on bioremediation technologies to deselenify soils, sediments and water of selenium by volatilization (Frankenberger and Karlson, 1991; Thompson-Eagle et al. 1991b; Frankenberger and Karlson, 1992; Thompson-Eagle and Frankenberger, 1992; Karlson and Frankenberger, 1993; Frankenberger and Karlson, 1994a; Frankenberger and Losi, 1995; and Losi and Frankenberger, 1997). Management factors affecting volatilization of selenium from sediments and water are summarized in Tables 1 and 2.

Frankenberger and his co-workers have conducted pioneer research in characterizing volatilization of selenium as a bacterial and fungal reaction. This transmethylation reaction involves homocysteine, methionine, cobalamin derivatives and reducing agents such as thiols including glutathione. Methylating microorganisms have been isolated in many sediments and evaporation pond waters throughout the SJV. The addition of protein sources as well as pectin can stimulate volatilization up to 300-fold of the native natural rate (Thompson-Eagle and Frankenberger, 1990). The primary product of selenium volatilization is dimethylselenide (DMSe) which is a nontoxic species as documented in acute toxicity studies. Selenium removal rates have been reported as high as 38 percent for protein-treated pond waters after 140 days. Volatilization can be inhibited at very high nitrate concentrations but sulfate has no effect on DMSe release. Laboratory studies with ⁷⁵Se-labelling were employed to identify optimum management practices to accelerate selenium volatilization. This bioremediation technology is highly dependent on specific carbon amendments (pectin and proteins), pH, temperature, moisture, aeration, and activators (co-factors). Selenium biomethylation is protein/peptide-limited rather than nitrogen-, amino-, or carbon-limited. Crude casein and its components, δ -, β -, and κ -caseins, and peptides are equally stimulatory producing greater than 50-fold enhancement in DMSe yield.

To demonstrate the viability of volatilization of selenium as an effective bioremediation technology to dissipate selenium from soil and sediments, Frankenberger (unpublished) has conducted an experiment where the San Luis Drain sediment was collected, homogenized and placed in mesocosms in the greenhouse. These mesocosms consisted of contained systems opened to the atmosphere with the sediment 6 inches deep. The treatments consisted of moist-only, application of ground orange peel and a protein mixture including casein and albumin. The contained sediments were mixed and stirred to promote aeration on an interval of twice a week. Figure 1 shows the decline in total selenium in the sediments on monthly intervals. It is evident from these data that orange peel and the protein mixture are more effective in promoting selenium volatilization. After 10 months, approximately 13.6 percent of the selenium was removed in the moist treatment compared to 37.0 percent upon the addition of orange peel and 45.8 percent when treated with the protein mixture. This study unequivocally demonstrates that selenium volatilization is a viable technology to remove selenium from soils and sediments. This desalinification procedure has been outlined in detail by a patent filed by Frankenberger et al. (1989).

Higher plants also possess the capacity to volatilize selenium (Lewis, 1971; Terry et al., 1992; Biggar and Jayaweera, 1993). This process occurs in both selenium-accumulator and non-selenium-accumulator plant species. Selenium non-accumulators typically release DMSe, while accumulators mainly volatilize DMDSe (Evans et al., 1968; Lewis, 1971). Generally, plant species differ substantially in their ability to volatilize selenium (Terry et al., 1992). Indian mustard and other *Brassica* species were found to be particularly effective volatilizers of selenium. There was evidence that the ability to volatilize selenium was associated with the ability to accumulate selenium in plant tissues (Terry et al., 1992). Recently, it has been shown that roots are the main sites of selenium volatilization in plants (Zayed and Terry, 1994). This is especially interesting since plant roots can be used to filter out selenium from polluted waters through uptake and accumulation in plant tissues in addition to volatilization. In fact, rhizofiltration, the use of plant roots to remove pollutants from water, is an emerging environmental cleanup technology, not only for selenium but also for many other trace elements and heavy metals (Dushenkov et al., 1995). Roots of many hydroponically grown terrestrial plants were shown to be effective in removing pollutants from water due to uptake and concentration in their tissues (Dushenkov et al., 1995). In the case of metalloids such as Se, volatilization provides an additional pathway of removal, which accelerates the rate of pollutant removal from water.

N. Biological Precipitation

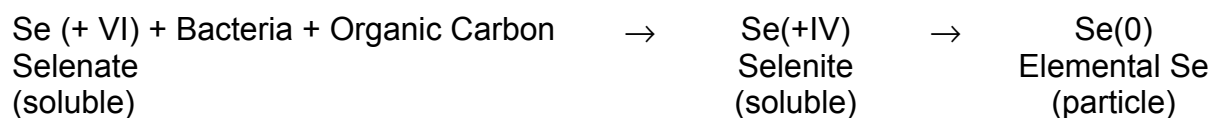
There are number of reports on microorganisms which can reduce selenooxanions into elemental selenium. However, in most cases, these bacteria exhibit low growth rates and require strict anaerobicity. Reduction may be inhibited by alternative electron acceptors such as NO_3^- which is common in seleniferous waste streams.

Recent work has suggested that certain facultative organisms are able to reduce SeO_4^{2-} under anaerobic or microaerophilic conditions. A recently isolated SeO_4^{2-} reducing organism, *Thauera selenatis* is reportedly a facultative anaerobe that reduces SeO_4^{2-} only while growing anaerobically (Macy, 1994). Losi and Frankenberger (1997b) have isolated a bacterium from the San Luis Drain (San Joaquin Valley, CA) identified as *Enterobacter cloacae* SLD1a-1 which is a facultative anaerobe and is capable of using NO_3^{2-} and SeO_4^{2-} as terminal electron acceptors during anaerobic growth. Nitrate does not seem to interfere with SeO_4^{2-} reduction by this organism.

Washed-cell suspension experiments with *Enterobacter cloacae* SLD1a-1 revealed that selenite is a transitory intermediate in reduction of SeO_4^{2-} being produced and rapidly reduced concomitantly. Nitrate is also reduced concomitantly and at a much higher rate than SeO_4^{2-} . Although this reaction is enzymatic, reduction of either oxyanion does not appear to be an inducible process. Recent studies have shown optimum conditions (including pH, temperature, and electron donors) for SeO_4^{2-} reduction and removal of selenium from drainage water by *Enterobacter cloacae* SLD1a-1 (Losi and Frankenberger, 1997b,c).

Enterobacter cloacae SLD1a-1 is capable of reducing selenate and selenite into dimethylselenide as well as precipitating the soluble oxyanions into an insoluble elemental selenium. This bacterium is active in volatilizing selenium under aerobic conditions and precipitates selenium into Se⁰ under anaerobic conditions. Thus under both modes of respiration (aerobic and anaerobic) it has two separate mechanisms for removing selenium out of its surrounding environment. Optimum management schemes can be manipulated to enhance either process in the removal of selenium from drainage water.

Several treatment technologies have been investigated that utilize selenium bioreduction to remove selenium oxyanions from solution with a goal of treating agricultural drainage water. An extensive review of these technologies has recently been presented by Losi and Frankenberger (1997a). Selenium present in drainage waters primarily exists in the soluble oxidized selenate form. By supplying an organic carbon source as an electron donor, selenium can be reduced to selenite and then to elemental selenium. Elemental selenium is a particulate and can be removed by conventional solid separation processes. This can be illustrated by the following pseudo reaction:



Because nitrate is also present in the drainage water, it is reduced through bacterial denitrification. Oxygen must be excluded from the reactor or reduction of nitrate and selenium will not occur. Because nitrate is present in much higher concentrations than selenium, most of the organic carbon is used for nitrate reduction. Reactor configuration influences the efficiency and speed of the conversion and so different types of reactors have been investigated.

Several pilot-scale projects that use anaerobic reduction reactions to precipitate selenium from drainage water have been tested. These treatment processes vary based on reactor design and the type of carbon source and nutrients provided to the microorganisms. Reactor designs include above ground tanks containing sludge beds, fluidized beds, or fixed films. The carbon sources that have been tested include methanol, Steffens waste from sugarbeet processing, acetate from acetic acid, and molasses. The most significant research and demonstration of selenium removal by biological processes in reactor systems has been conducted by EPOC AG at Murietta Farms, Dr. Joan Macy, University of California, Davis, and Engineering Research Institute (ERI) at California State University, Fresno, CA. In studies conducted by those listed above, the following conclusions can be reached.

1. Soluble selenium in drainage water can be reduced from 300 or 500 ppb to 30 ppb or less.
2. A two-stage reactor system with a total hydraulic detention time on the order of a few hours appears to be an effective combination. The upflow anaerobic sludge blanket reactor (UASBR) followed by a fluidized bed reactor is particularly well-suited to treating drainage water because of this combination's ability to handle inorganic precipitation.
3. The total cost for one million gallons per day would be estimated at \$440 to \$520 acre-foot of water treated, with operating costs representing \$340 to \$420 acre-foot. The cost for the organic carbon that is added to the water accounts for 25 to 5 percent of the operating costs if methanol is used.

The advantages of the biological precipitation reaction are (i) soluble selenium can be reduced by up to 95 percent, (ii) low production of solid residuals for disposal due to slow anaerobic growth rates, (iii) low required detention time allows use of standard engineering sizes of treatment systems, and (iv) the system is enclosed with no exposure to the environment or wildlife. The major disadvantage of this technology is that soluble selenium residual of 30 ppb or greater is likely from biological treatment only and organic carbon costs are high unless low cost alternatives can be used.

O. Flow-Through Wetlands

Constructed wetlands constitute a complex ecosystem, the biological and physical components of which interact to provide a mechanical and biogeochemical filter capable of removing many different types of contaminants from water. They have been used to cleanup municipal wastewater, stormwater runoff, and many other types of polluted wastewaters in the USA and in Europe (Kadlec and Knight, 1996). Constructed wetlands are orders of magnitude lower in cost than other treatment systems; however, the science of understanding wetland selenium detoxification mechanisms is in its infancy.

There is evidence that significant losses of Se, through biologically mediated methylation and volatilization, can occur in wetlands. The toxicity of the volatile selenium compounds, such as dimethylselenide (DMSe), are 600-700 times lower than the inorganic forms (Karlson and Frankenberger, 1988). Finding the conditions that are optimum for volatilization has been one of the goals of constructed-wetland studies. Concerns over low volatilization rates of DMSe from aquatic systems and the gradual accumulation of selenium in the sediments and vegetation may limit this method. The attractiveness of this method is the low cost and large volumes of water that could be treated. The biggest concern with wetland treatment systems is the potential use by waterfowl and the similarity to the conditions that existed at Kesterson Reservoir.

One indication that wetlands might be useful in the removal of selenium from wastewaters came from a study of a 36-hectare constructed wetland located adjacent to the San Francisco Bay, California. Some Bay area oil refineries have discharged into the Bay wastewater containing selenite at levels that substantially exceed those permitted under the guidelines established by both state and federal regulators.

Chevron has supported research directed by Norman Terry at UCB to determine the feasibility of wetlands in removing selenium from their wastewaters. Analysis of the wetland inlet and outlet waters showed that the constructed wetland was successful in removing 89 percent of the selenium from the wastewater passing through it. Inflow selenium concentrations of 20-30 $\mu\text{g L}^{-1}$ decreased to $<5 \mu\text{g L}^{-1}$ in the outflow (Hansen et al., 1998). The fact that the Chevron wetland was processing up to 10 million liters of oil refinery effluent each day strengthens the significance of the role of constructed wetlands in removing selenium from large volumes of wastewater.

Constructed wetlands remove selenium by reduction to insoluble forms which are deposited in the sediments, by accumulation into plant tissues, and by volatilization to the atmosphere, i.e., through biological volatilization of plants, plant/microbe associations and microbes alone. Cooke and Bruland (1987) estimated that as much as 30 percent of selenium introduced into the ponds of Kesterson Reservoir in the SJV of California was lost by volatilization into the atmosphere through biomethylation and that the process varied seasonally. Allen (1991) tested the ability of a constructed wetland to remove selenium from water spiked with selenite. She found that the rate of selenium removal by the wetland exceeded 90 percent of the total selenium introduced and considered that biological volatilization was an important component of this loss. Recently, Zhang and Moore (1997) examined the role of volatilization in the removal of selenium by a wetland system, using wetland microcosms spiked with different forms of selenium. Their results indicate that natural selenium volatilization is an important process removing selenium from wetland systems. Sediment and plants were the major producers of volatile selenium from the system. Actual field measurements of selenium volatilization performed by N. Terry and his co-workers have shown that biological volatilization might have accounted for as much as 10-30 percent of the total selenium removed from the San Francisco Bay constructed wetland (Hansen et al., 1998). They measured rates of selenium volatilization as high as 330 $\mu\text{g m}^{-2}$ soil surface day⁻¹ from areas vegetated with rabbitfoot grass. Thus, it appears that biological volatilization of selenium is a significant pathway of selenium removal in wetlands.

The success of the San Francisco Bay constructed wetland in removing selenium inspired a group of scientists under the auspices of the University of California Salinity/Drainage Task Force to initiate a flow-through wetland at the Tulare Lake Drainage District site in the spring of 1996. The purpose of this trial was to test the effectiveness of the flow-through wetland in removing selenium from selenium-laden agricultural drainage waters before discharge into the evaporation basins. Ten rectangular wetland cells, each 250 x 50 ft in dimension, were constructed. The wetland cells were then flooded and planted with various types of vegetation such that each cell contained one or more of the following plant species: salt marsh bulrush, baltic rush, cattail, cord grass, rabbitfoot grass, saltgrass, tule, and widgeon grass. One cell was left without plants as a control natural cell. By the summer of 1997, all except the open water cells were established with vascular plants. These wetland cells are currently being monitored in order to evaluate their performance in selenium removal from agricultural drainage waters containing relatively low levels of selenium (20-30 $\mu\text{g L}^{-1}$). Surface water, sediment pore water, plant tissue, and sediment samples are being collected monthly to determine the removal efficiency, fate of selenium, and the oxidation state of water soluble selenium (Terry, 1997). Plexiglass chambers that cover whole plants are being used to monitor selenium volatilization rates. Preliminary

data suggest that 21 percent to 89 percent of the incoming selenium is being removed from the drainage water. Work is ongoing to determine the relative partitioning of selenium into sediments, plant biomass, and gaseous losses. To evaluate selenium transfer through the food chain, analysis of selenium load in primary producers and representative invertebrate species is underway. The most recent results show that: i) the wetland cells are capable of significantly reducing the concentrations of selenium in drainage water, ii) the most efficient cell in reducing selenium was that planted with cattail and widgeon grass, and iii) the efficiency of the wetland in removing selenium appears to be increasing from 1997 to 1998.

In conjunction with this field-scale project, a mesocosm-scale project is ongoing at U.C. Riverside. This project is designed to address some of the shortfalls of the field-scale project which include non-replication and an inability to measure leaching losses. The mesocosm wetlands consist of polyethylene drum-halves linked in series and filled with 30 cm of soil. Three drum-halves are linked in a cascade design to represent the beginning, middle, and end of a long, narrow wetland cell. Twelve mesocosm series allow for 4 treatments with 3 replications. In the first part of the study, the treatments were cattails, rabbitsfoot grass, a shallow water control, and a deep water control (no vegetation). Preliminary analysis of the influent and effluent indicates that the cumulative selenium load was reduced by 42 percent in the vegetative treatments and 28 percent in the non-vegetative treatments. No significant difference in total selenium reduction was observed between the two vegetation types (Parker et al., 1997). Preliminary results on the non-vegetative treatments suggest that about half of the loss could be attributed to volatilization.

P. Subsurface Flow Wetlands

Constructed subsurface flow (SSF) treatment wetlands can also be used to remove selenium from irrigation drainage water. These treatment wetlands systems would be especially effective where selenium concentrations and loadings are high and flow volumes are low. The wetland would consist of gravel beds that serve as the rooting medium for salt-tolerant emergent wetland plants (such as bulrush), with the agricultural drainage water flowing through the gravel (Fig. 2). As the water flows through the gravel bed, oxidation-reduction processes in the plant root zone (especially due to the interactions of the microbial community and the plant roots) would remove selenium through a combination of uptake and volatilization. These processes are well understood for treatment of conventional pollutants in wastewater (Kadlec and Knight, 1996), and the same principles, coupled with knowledge about the oxidation-reduction cycling and volatilization of selenium (e.g., Frankenberger and Karlson 1994b, Oremland 1994, Terry and Zayed 1994), could be applied to treatment of selenium in agricultural drainage water.

Besides reducing selenium in drainage water to safe levels, another advantage of this technology would be the development of a treatment system that can be constructed within individual sumps or agricultural drains so the loss of arable land would be minimized. The primary advantage of subsurface flow treatment wetlands are that they reduce the potential for an aquatic food chain pathway for selenium exposure to fish or birds.

The SSF treatment system will optimize volatilization through microbial-mediated reactions as the primary removal mechanism. This technology could also evaluate the potential of a specific bacterium, *Enterobacter cloacae* SLD1a-1, that has been shown to be effective in removing selenium from agricultural drainwater with little or no inhibitory effect of nitrate. Thus, the use of a replaceable, selenium-adsorptive or -precipitative treatment medium could be evaluated in comparison to (or integration with) a volatilization-based removal system.

III. CONCLUSIONS

This review evaluates the most recent findings on treatment technologies in removal of selenium from agricultural drainage water. New recent advances have been made in many technologies since the Agricultural Drainage Treatment Technology review was released in July 1998 by the San Joaquin Valley Drainage Program. The environmental impact of selenium and other trace elements in the SJV drainage water was not fully recognized until about 1985, when high levels of selenium were identified in biota in Kesterson Reservoir. However, long before the selenium problem emerged, drainage water reclamation was being seriously considered at the tubular reverse osmosis plant in Firebaugh in the early 1970s. The motivation for construction of this experimental facility arose from two fundamental issues relevant to SJV agricultural drainage. Of primary concern was augmentation of irrigation water supplies by drainage water desalinization. This was indeed a challenging application of the emerging technology under development at the time. A second goal was directed towards reduction of drainage water volume. Management of salt accumulation could then be enhanced by such waste minimization technology.

These goals are especially relevant nearly 30 years later. State-of-the-art membrane technology has developed to a point where economical desalinization of drainage water should be considered. In addition, solar pond technology, the potential which has not been adequately explored, should be seriously considered from a perspective of salt management as well as energy production. These technologies certainly play important roles in desalinization and salinity control in future management of drainage water. Recently, U.S. Filter Corporation has demonstrated a microfiltration technology in testing its ability to remove selenium and nitrates from the Alamo River in the Imperial Valley, with the primary goal of recycling the agricultural drainage as irrigation water equivalent to the quality of the Colorado River. Although many of these physical technologies are quite promising in removing selenium and other toxic ions from the water, their cost is prohibitive on a large scale application.

Chemical reduction of selenium with zero valent iron and ferrous oxides is less effective in water of high redox potential.

Biological treatment holds the most promise because of its cost effectiveness and permanent removal of selenium from the matrix. Bacteria, plants and micro-algae active in selenium precipitation and volatilization are the most promising players in remediation of drainage water. Previous studies have shown that in aquatic systems the major mechanism of removal of selenium is through reductive precipitation. The major problem with volatilization of selenium, particularly from water, is that the methylated selenium species are water-soluble and thus their release into the atmosphere is subject to entrapment.

In reviewing each of these treatment technologies, it is imperative to note that exciting advances are being made on a short-term investment. These biological systems serve as biogeochemical filters capable of removing selenium through assimilation, bacterial precipitation, and volatilization. Technologies should be promoted that are cost-effective and pose the least threat to the environment with safety to birds and other wildlife. Mass balances should be very carefully calculated to understand the mechanism of selenium removal. With intense research in treatment technologies, perhaps a combination of biological, chemical and physical techniques may be useful in development of a cost-effective strategy in treatment of agricultural drainage water.

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Table 1. Management factors affecting volatilization of selenium from soil and sediments.

Management Factors	References
<p>Selenium volatilization after 37 days was increased 1.2-fold at a C/N = 20, 1.1-fold at C/N = 10, and decreased by 11.8 percent at C/N = 5.</p> <p>Nitrogen applications of high rates can inhibit Se volatilization.</p> <p>Total volatilization over 21 days was increased 2.5-fold with Co, 1.67-fold with Zn, and 1.46-fold with Ni at 25 mmol kg⁻¹.</p>	Karlson and Frankenberger (1988)
<p>Three fungal isolates including <i>Acremonium falciforme</i>, <i>Penicillium citrinum</i>, and <i>Ulocladium tuberculatam</i> were isolated from seleniferous soils active in Se volatilization.</p> <p>Without carbon amendments, volatilization rates were up to an order of magnitude higher with Se(IV) as the Se source when compared to Se(VI).</p> <p>Carbon addition in the form of pectin accelerated Se evolution 2- to 130-fold which was more pronounced with Se(VI).</p> <p>With carbon amendments, Se(VI) is volatilized almost as rapidly as Se(IV) from all soils.</p> <p>With pectin amendments over a period of 118 days, total Se volatilization ranged from 11.3 to 51.4 percent of the added Se.</p> <p>A minimum Se threshold for alkylselenide production was not found, applying Se additions as low as 10 µg kg⁻¹ soil.</p>	Karlson and Frankenberger (1989)
<p>A saline (>20 dS m⁻¹) seleniferous soil collected from Pond 4, Kesterson Reservoir was assayed for DMSe production by incubating for up to 120 hours at 22°C. Optimum conditions for Se volatilization were observed at pH 8; moisture content, field capacity; temperature, 35°C; L-methionine, 100 mg kg⁻¹ soil; galacturonic acid, 3.6 g C kg⁻¹ soils; and protein sources including casein (2.0 g C kg⁻¹ soil) and albumin (0.05 to 2.0 g C kg⁻¹).</p> <p>Albumin applied to soil enhanced gaseous Se production 19.3-fold over the unamended control.</p>	Frankenberger and Karlson (1989)

Atkinson et al. (1990)	<p>The photolysis and kinetics of DMSe with OH and NO₃ radicals and O₃ was determined. DMSe is not subject to photolysis. Rate constants for reaction with OH radical and O₃ were 6.78 x 10⁻¹¹ and 6.80 x 10⁻¹⁷ cm³ molecule⁻¹ s⁻¹.</p> <p>The rate constant for the reaction with NO₃ radical was calculated at 1.4 x 10⁻¹¹ cm³ molecule⁻¹ s⁻¹.</p> <p>Combining these rate constants with estimated an ambient tropospheric concentrations of OH and NO₃ radicals and O₃, leads to the following calculated lifetimes of DMSe: OH radicals, 2.7 h; NO₃ radicals, 5 min. and O₃, 5.8 h.</p>
Calderone et al. (1990)	<p>A sediment column study established a Se₀ (Se volatilization potential) and rate constant (Se volatilization rate coefficient) derived from a first-order kinetic model).</p> <p>Increasing the temperature from 15 to 35°C promoted volatilization of Se (Q₁₀=1.96)</p> <p>The amount of Se leached out of the sediment was independent of the initial total Se inventory.</p> <p>Volatilization of Se followed a first-order reaction and was highly dependent on the initial Se concentration.</p> <p>The addition of organic amendments promoted volatilization of the Se being less available for leaching. The application of gluten, a wheat storage protein, was found to enhance volatilization of Se 1.7 to 3.2-fold over the control more strongly than any other treatment including casein, orange peel, and cattle manure.</p>
Karlson and Frankenberger (1990)	<p>With Kesterson sediment, the highest Se removal by volatilization resulted from the combined application of citrus peel and ZnSO₄ (44 percent) followed by citrus peel alone (40 percent), and citrus peel combined with an ZnSO₄, (NH₄)₂ SO₄ and <i>Acremonium falciforme</i> (30 percent).</p> <p>With an evaporation pond sediment obtained from the Peck Ranch, the highest amount of Se removed was obtained with chitin (29 percent), cattle manure (29 percent) and citrus peel alone (27 percent) after 273 days. Without amendments, 14.0 percent of the native Se was volatilized in 273 days.</p>

Karlson et al. (1994)	<p>The vapor pressure of volatile Se gases as determined using an isotenoscope method were calculated at 32.0 and 0.38 kPa for DMSe and DMDSe, respectively, at 25°C.</p> <p>The enthalpies of vaporization were calculated at 31.9 and 74.9 kJ mol⁻¹, respectively.</p> <p>The solubility of DMSe is 0.024 g/g of water.</p> <p>The Henry's Law constant for DMSe was calculated as 143 kPa kg mol⁻¹ (0.144 kPa m³ mol⁻¹)</p>
Frankenberger and Karlson (1994b)	<p>Laboratory studies revealed that selenium volatilization rates were higher under continuously moist conditions (-33 kPa) compared with wetting and drying cycles.</p> <p>Optimum aggregate size to promote volatilization of Se was 0.53 mm when compared to 0.15, 1 and 2 mm.</p> <p>The application of saline well water (7.5 dS m⁻¹ over six months compared with deionized water had little affect on volatilization rates of Se from a highly saline (22 dS m⁻¹) seleniferous dewatered sediment.</p>
Frankenberger and Karlson (1995)	<p>A field study demonstrating volatilization Se from a dewatered seleniferous sediment revealed that after 22 months, the application of water plus tillage alone removed 32 percent of the Se while cattle manure removed 58 percent.</p> <p>Among the parameters which enhanced volatilization of Se were an available C source, aeration, moisture, and high temperatures.</p>
Rael and Frankenberger (1995)	<p>Selenomethionine was discovered in the fulvic fraction of a seleniferous sediment as detected by selected ion-monitoring by GC-MS.</p>

<p>Products of atmospheric important reactions of DMSe revealed that dimethyl selenoxide $[(CH_3)_2SeO]$ is a major product of the gas-phase reaction of DMSe with ozone, with an estimated yield of approximately 90 percent.</p> <p>Significant fragmentation via Se-C bond breakage occurred during the reactions of DMSe with the OH radical and the NO_3 radical as indicated by HCHO formation yielding approximately 40 and 60 percent, respectively.</p>	Rael et al. (1996)
<p>A long-term field experiment was carried out at Kesterson Reservoir to determine optimum management factors removing selenium from soil.</p> <p>Over a period of 100 months, 68 to 88 percent of the total selenium was dissipated from the topsoil (0-15 cm).</p> <p>The pattern of Se depletion in soil was not correlated with rainfall events nor with temperature.</p> <p>The highest amount of Se depletion occurred with the amendment of the protein, casein.</p> <p>A two-compartment model was superior to a one compartment model for describing the long-term kinetics of Se depletion in the soil.</p> <p>The rate of Se depletion was initially faster than at later times indicating that a rate limiting mechanism changed during the time of the study.</p>	Flury et al. (1997)

Table 2. Management factors affecting volatilization of selenium from water.

Management Factors	References
<p>Natural formation of DMSe in evaporation pond water was less than 1 percent of the total Se inventory after 40 days of incubation.</p> <p>No Se methylation took place in autoclave, unamended pond water.</p> <p>L-Methionine (10 μM) stimulated DMSe production in nonsterile evaporation pond water.</p> <p>Increasing the temperature to 35°C and the addition of 1 percent glucose with a fungal inoculum, <i>Alternaria alternata</i>, doubled DMSe production over the controls after 25 days of incubation.</p> <p>Carbon sources such as glucose, maltose, sucrose, and galacturonic acid at 2 g C L⁻¹ under ambient conditions slightly enhanced indigenous Se volatilization (1.5-fold).</p> <p>Of the amino acids tested, L-methionine (0.02 g C L⁻¹) stimulated the DMSe evolution from pond water more so than L-cysteine, L- cystine, and L-serine.</p> <p>The proteins, egg albumin, casein, and gluten (2 g C L⁻¹) dramatically increased Se volatilization causing a 23, 41, and 10 percent Se loss from the inventory, respectively after 43 days of incubation.</p>	Thompson-Eagle and Frankenberger (1989a).
<p><i>Alternaria alternata</i> was isolated from water samples collected from evaporation pond facilities in the San Joaquin Valley.</p> <p>The optimum pH and temperature for methylation of Se were 6.5 and 30°C, respectively.</p> <p>Selenate and selenite were methylated more rapidly than selenium sulfide and various organic Se compounds (6-selenoguanosine, 6-seleninosine, seleno-DL-methionine, 6-seleno purine).</p> <p>L-Methionine and methyl cobalamine (0.1 μM) stimulated DMSe production.</p>	Thompson-Eagle et al. (1989b)

<p>Laboratory studies showed that Se volatilization is protein-peptide limited rather than nitrogen-, amino acid-, or carbon-limited.</p> <p>Protein sources including cottonseed meal, cheese whey and yeast sludge dramatically increased Se volatilization (29-fold, 300-fold and 41-fold, respectively) over unamended water samples, with over 10 percent of the Se inventory converted into DMSe in 17 days.</p> <p>A single casein amendment (0.2 g C L^{-1}) to water columns in the field caused a 38 percent Se loss from the initial inventory of a San Joaquin Valley evaporation pond in 142 days.</p>	Thompson-Eagle and Frankenberger (1990a)
<p>Biomethylation was optimal in well-mixed, aerobic system amended with a protein source.</p> <p>Cofactors ($10 \mu\text{M}$ homocysteine and $10 \mu\text{M}$ reduced glutathione) enhanced production of DMSe in peptone-amended pond water.</p> <p>The species of inorganic Se present, SeO_3^{2-} and SeO_4^{2-} had little affect on the methylation efficiency.</p> <p>Increasing the Se concentration to 2, 4, 12, 22, or 102 mg Se L^{-1} in peptone-amended pond water decreased the percentage of Se removed from 8 to 4, 2, 1.3, 0.7 and 0.1 percent, respectively.</p> <p>The addition of casein (4 g L^{-1}) increased bacterial numbers 1,000-fold and stimulated Se volatilization 25-fold.</p>	Thompson-Eagle and Frankenberger (1991a).
<p><i>Aeromonas veronii</i>, isolated from a seleniferous agricultural drainage water, metabolized peptone and was active in volatilizing Se principally as DMSe.</p> <p>Other volatile products included dimethyl disulfide, methyl selenol, dimethyl selenosulfide, and dimethyl diselenide.</p> <p>The rate of Se volatilization correlated with the growth of <i>A. veronii</i> with the highest levels of DMSe released during the exponential phase of growth.</p>	Rael and Frankenberger (1996)